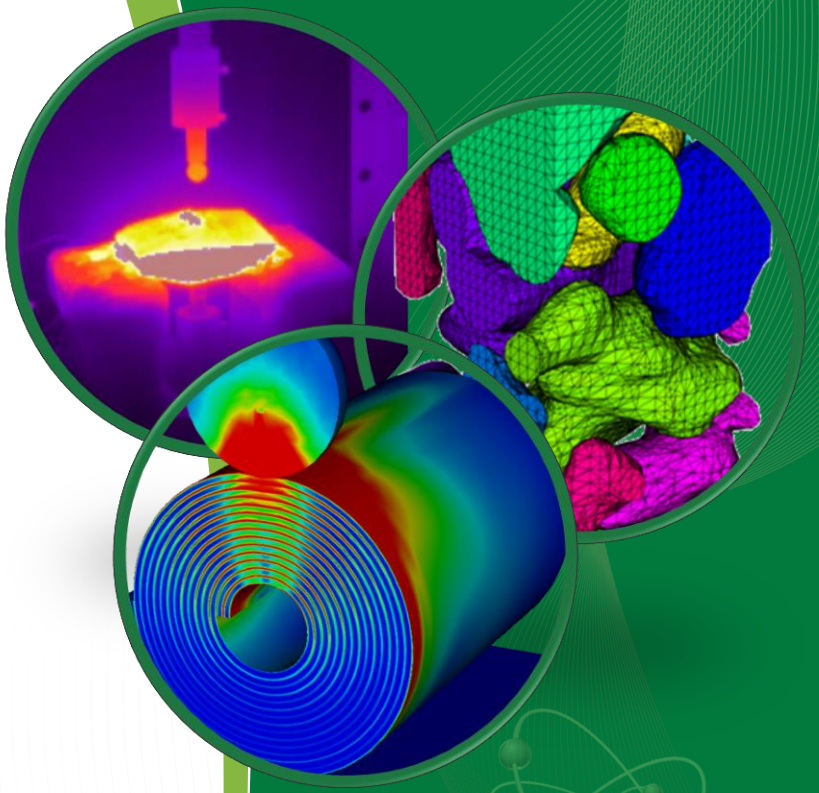
Microstructure imaging and electrolyte transport property measurement for mathematical modeling



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Team: CABS

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June 20, 2018 **Project ID:** bat302

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CABS Consortium for Advanced Battery Simulation

OAK RIDGE National Laboratory | Argonne NATIONAL LABORATORY | BERKELEY LAB | Sandia National Laboratories

Overview

Timeline

- Project start date: October 2015
- Project end date: September 2018
- Percent complete: 92%

Barriers Addressed

- High cost
- Low performance

Budget

- FY 17:
  - Total CABS funding: 2225K
  - This effort: 630K
- FY 18
  - Total CABS funding: 1398K
  - This effort: 228K

Partners

Outside VT

Kee Sung Han (PNNL/EMSL)

Inside VT

Sergiy Kalnaus (ORNL)
Xianghui Xiao (ANL/APS)
Andrew Jansen (ANL/CAMP)
Vince Battaglia, Gao Liu (LBNL)

Relevance

- Objective: Provide accurate simulation input data for CAEBAT teams, enabling construction of accurate models to guide cost and performance optimizations
- Specifically, the objectives of FY18 are to
  - Obtain image data for cycled electrodes
  - Quantitatively analyze image data for cycled electrodes
- Correlating images and electrochemical data will help to calibrate models and could reveal unanticipated phenomena.
  - By supporting improved model accuracy, this project will help in the optimization of batteries to address the barriers of high cost and low performance

Approach

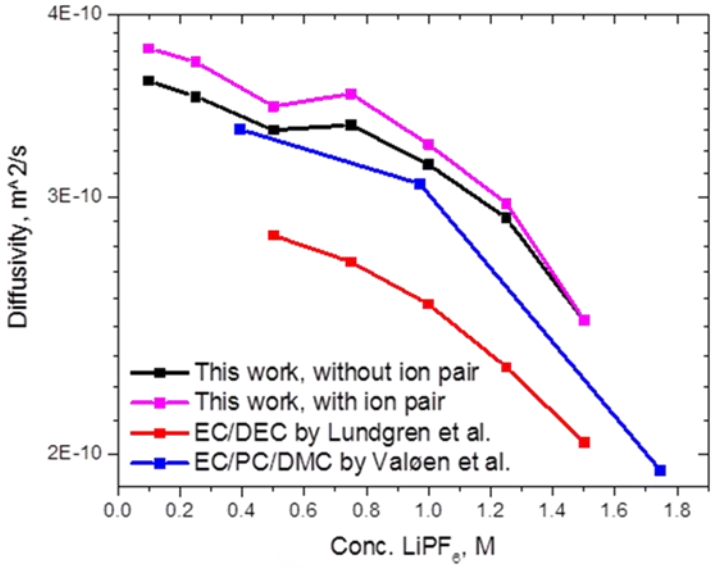
- Overall technical approach
  - Using NMC532 electrode fabricated by CABS partner (Sergiy Kalnus, ORNL), build pouch cell suitable for imaging by hard X-ray microtomography
  - Mount cell vertically in beamline to avoid difficulties with precisely aligning cell with horizontal plane, although at the cost of complicating postprocessing
  - Obtain *in operando* images rather than using cycled electrodes extracted from cells
  - Quantitative comparison of images taken at different times will require sophisticated postprocessing to perform alignment, correcting for sample movement
  - Build on techniques developed earlier for our TomPost library (https://sites.google.com/a/lbl.gov/tompost/) to perform image postprocessing
  - Incorporate new techniques into updated version of TomPost library

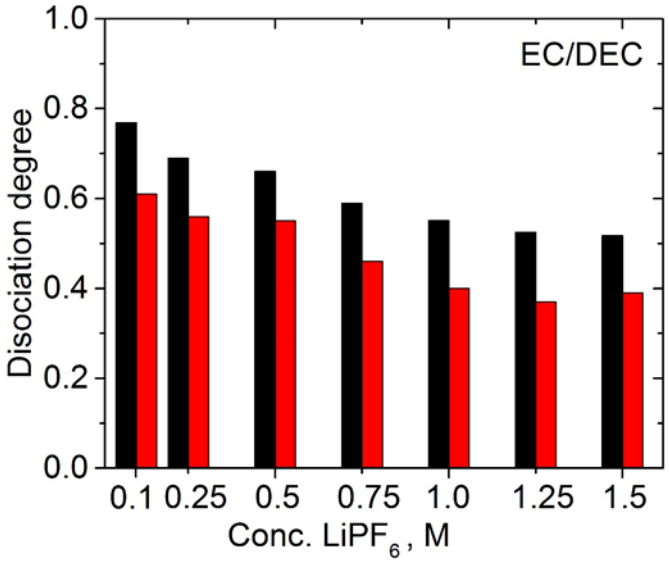
- FY18 milestones:
  - CABS: Obtain electrode image data from cycled electrode material
  - "CD-adapco" subproject: Develop postprocessing pipeline for tomographic reconstructions of cycled electrodes

FY17 Technical Accomplishments

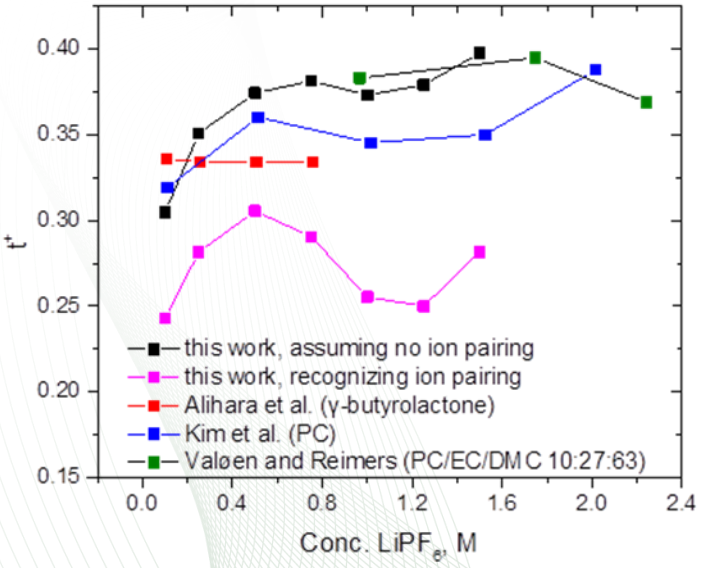
- Electrolyte solution (LiPF6 in EC/DEC, 1:1 by mass) self-diffusivity data obtained by pulsed field gradient NMR (Kee Sung Han, PNNL/EMSL)

Combined with ionic conductivity to yield degree of dissociation and corrected transport property values, meeting project objective of providing accurate simulation inputs





Black bars: Haven ratio
Red bars: Generalized Darken relation and concentrated solution theory



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FY18 Technical Accomplishments and Progress

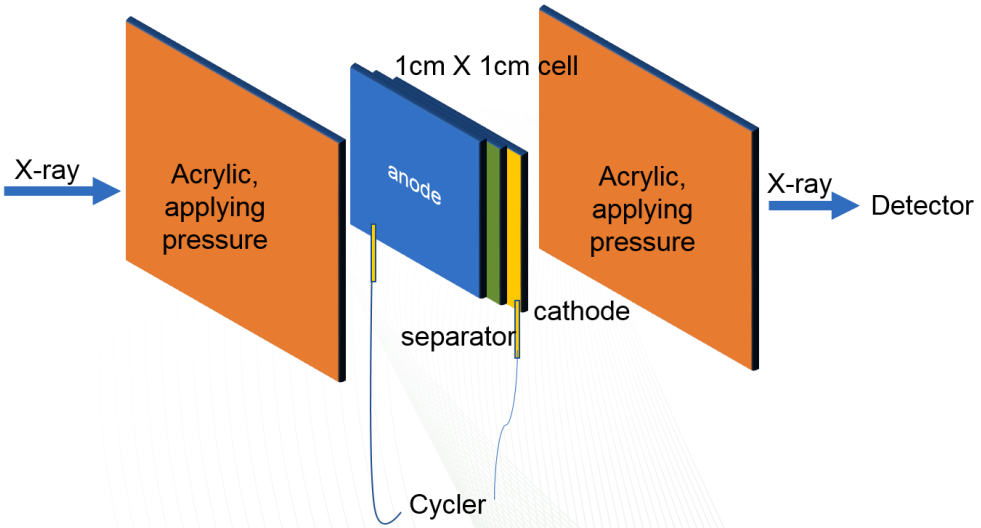
- FY16: Electrode fabricated by Sergiy Kalnaus, ORNL, using NMC532 active material
  - Estimated 40% porosity
- One pouch cell assembled at Cell Analysis, Modeling, and Prototyping (CAMP) Facility at ANL (Andrew Jansen)
  - 1 cm^2 NMC532 cathode paired with lithium anode
  - Electrolyte solution: 1M LiPF6 in EC/DEC (1:1 by mass)

Constructed pouch cell suitable for *in situ* X-ray microtomography imaging, to exceed imaging objective

FY18 Technical Accomplishments and Progress

- Pouch cell imaged at APS 2-BM (beamline scientist Xianghui Xiao)
- Region of interest restricted to NMC electrode
- Pouch cell sandwiched between rigid acrylic plates
- Mounted approximately vertically on rotating sample platform

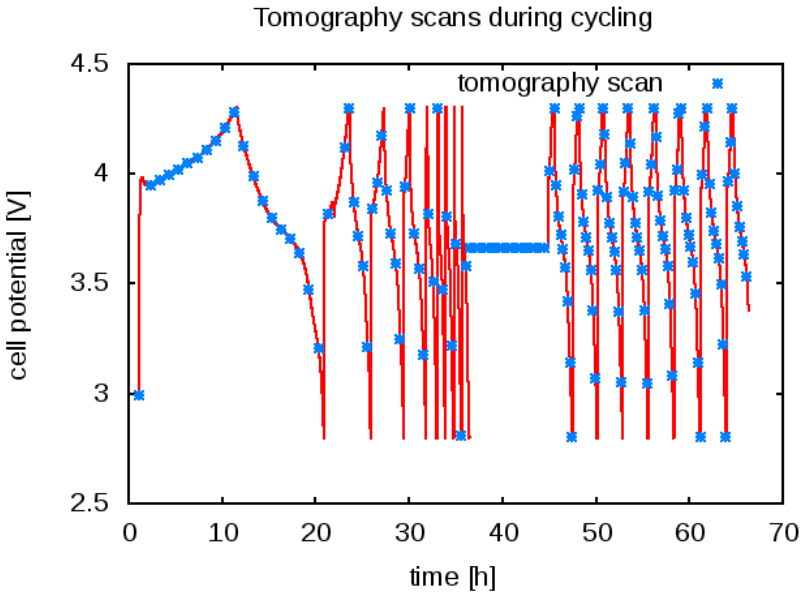
  - Advantage: rigid plates do not need to be perfectly perpendicular to axis of rotation to avoid obscuring NMC electrode
  - Disadvantage: postprocessing needed to align reconstructed electrode with voxel planes



Pouch cell mounting strategy devised for APS 2-BM

FY18 Technical Accomplishments and Progress

- Galvanostat leads with sufficient length and flexibility connected to pouch tabs
- Image acquisition started before electrochemical data acquisition, but with synchronized clocks
- 0.1C to 5C rates (10C not sustained)
- 152 tomography data sets obtained over 66 hours of cycling

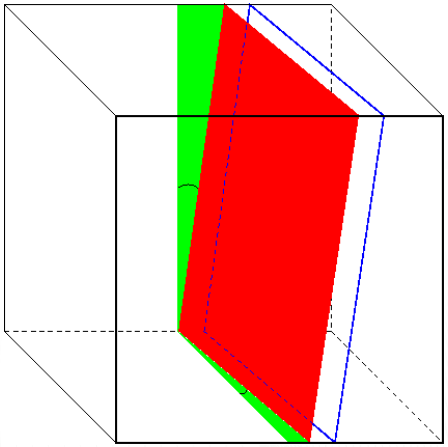


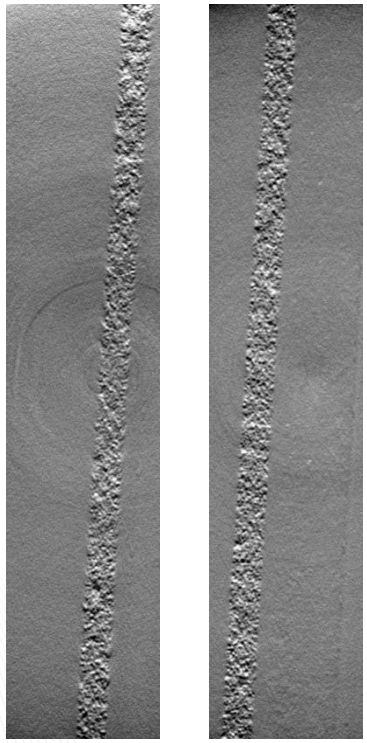
In operando imaging performed on pouch cell, exceeding the milestone of imaging a cycled electrode

FY18 Technical Accomplishments and Progress

Automated postprocessing required for quantitative analysis of image data

- Sample slightly angled and reconstructions show slight movement of sample throughout experiment
  - For comparison, electrode regions must be aligned through virtual translation and rotation
- Automation
  - Exactly documents postprocessing
  - Reduces influence of visual subjectivity
  - Saves time (152 data sets)



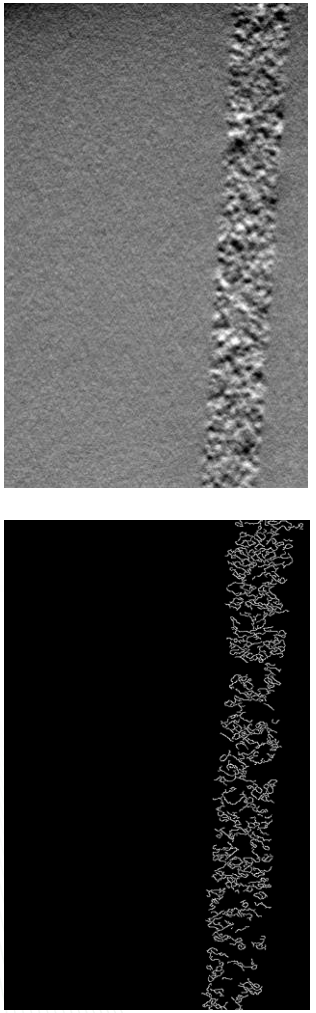


Start and end of experiment, 315 microns across

FY18 Technical Accomplishments and Progress

- Average voxel values in electrode region and surroundings are very similar
  - But electrode region is less spatially uniform
- Use Canny edge detection algorithm (from SciPy)
  - Effective detection parameters found by trial-and-error, same parameter values work for all data sets since images are similar
- Performed only for bounding slices of each data set
  - Electrode is nearly planar

Automated edge detection highlights electrode region

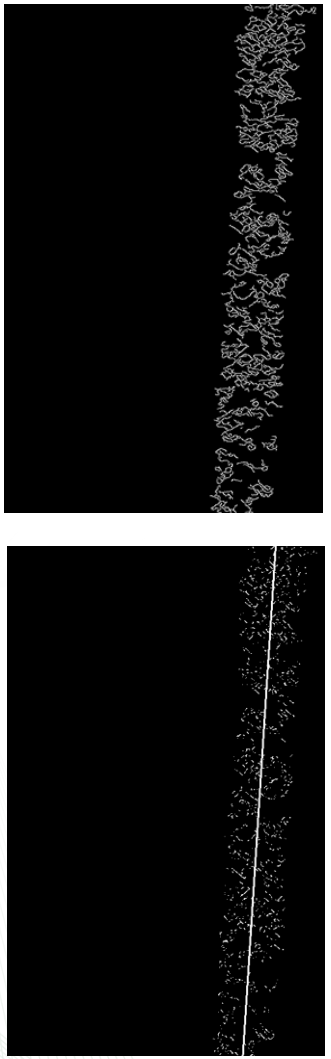


Images shown are 320 microns across

FY18 Technical Accomplishments and Progress

- Pixels within electrode are highlighted, but need higher-level detection of electrode as a planar unit
- Monochrome image with Canny edges filtered to emphasize regions with “bright” edge pixels
- Image reinterpreted as data points in Cartesian space
- Linear least-squares fit with linear function approximately identifies electrode central plane

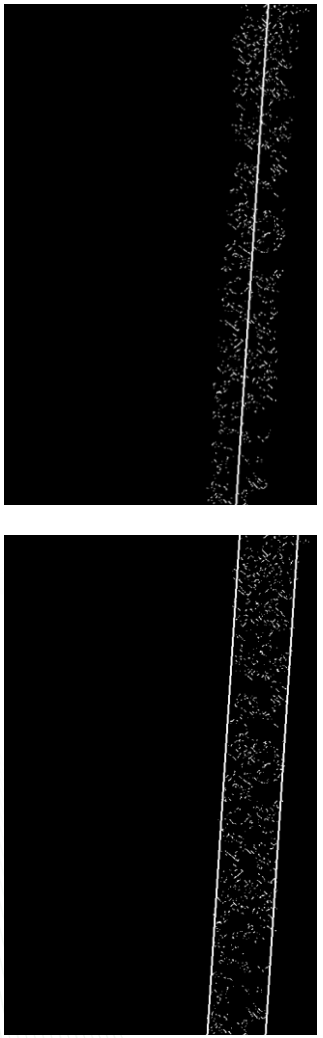
Have automated method for detecting central plane through electrode region



Images shown are 320 microns across

FY18 Technical Accomplishments and Progress

- Electrode has nearly uniform thickness, edges should be approximately aligned with central plane
- Walking across image, pixel value sums computed along lines parallel to central plane
- Sharp changes in sums, detected by k-means clustering (kmeans2 in SciPy) correspond to electrode edge locations

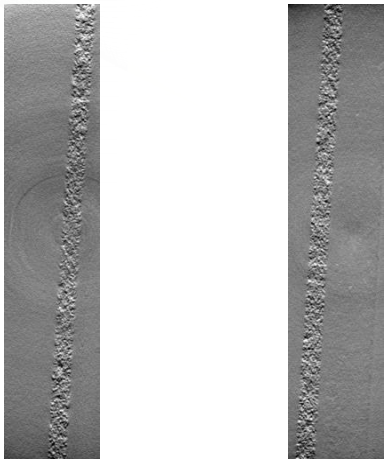


Images shown are 320 microns across

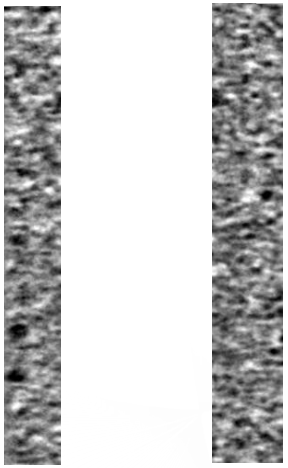
Have automated method for identifying boundaries of electrode region

FY18 Technical Accomplishments and Progress

- Having identified electrode surface planes, reconstructions are rotated and cropped



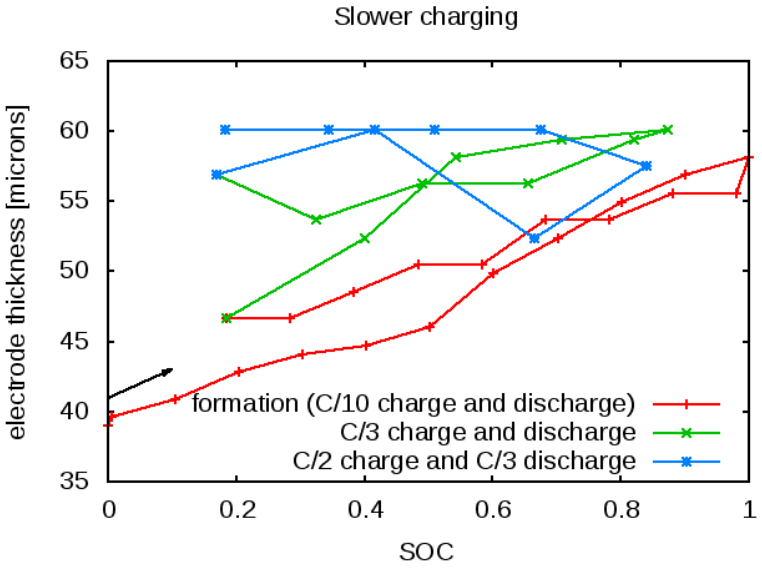
Start and end of experiment, 315 microns across

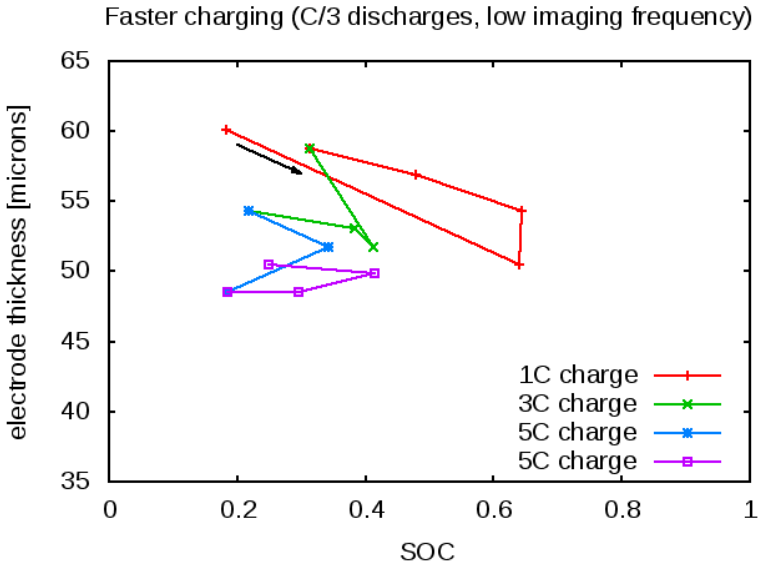


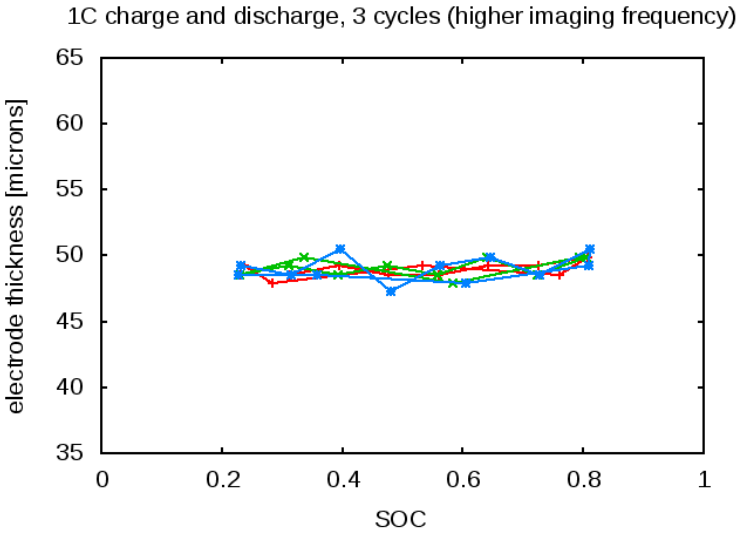
After processing (images shown are 320 microns tall)

Developed automated transformation of reconstructions into consistent blocks, fulfilling second milestone and enabling unprecedented quantitative comparisons of corresponding imaging and electrochemical data

FY18 Technical Accomplishments and Progress



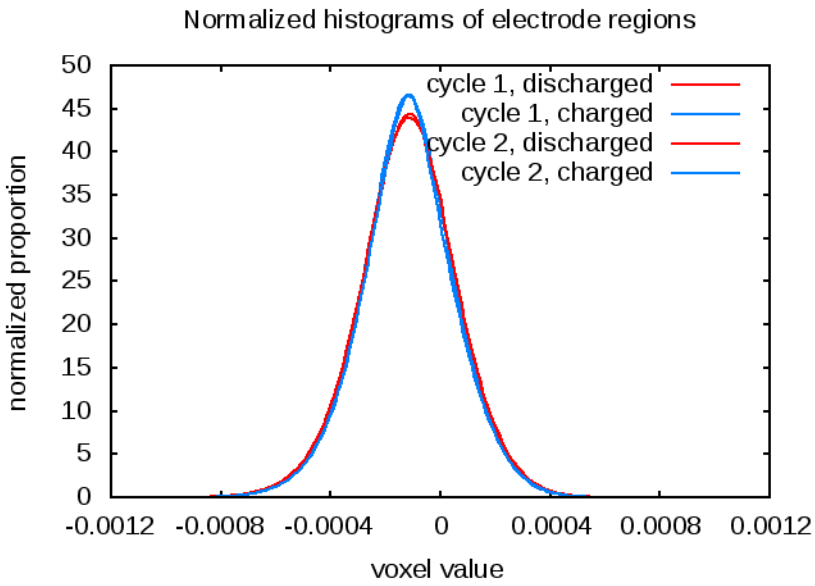




Clear correlation between electrode thickness and SOC only in initial cycles with slow charging; this offers unique information for modelers working to incorporate realistic strain into battery simulations

FY18 Technical Accomplishments and Progress

- Histograms of voxel values show slight but consistent variation with SOC in slow, initial formation cycles
- Voxel values approximately correlated with X-ray absorption / material identity



Histogram variation with SOC suggests changes in electrode density distribution, to be investigated further

Responses to Previous Year Reviewers' Comments

- Reviewer 6 asked about modeling details and about whether diffusion through a medium is being calculated or merely self-diffusion. This project does not involve modeling, but rather produces experimental data to support modeling efforts by our teammates. Our efforts have included some theoretical work to interpret the self-diffusivity data obtained by pulsed field gradient NMR in terms of the transport properties needed to apply concentrated solution theory.

- Reviewers 4 and 5 inquired about the role of the CD-adapco company. CD-adapco software and support was used in FY16-17 under the "CD-adapco" subproject in order to compare traditional macroscale simulations with simple corresponding microscale simulations. The "CD-adapco" subproject has transitioned to custom software development for tomography postprocessing. CD-adapco software is no longer being used and this project no longer contains a continuum simulation component.

- Reviewer 4 suggested performing MD simulations in order to better understand the diffusivity measurements. While this could provide further insight, we believe that the effort to develop this capability with the remaining resources will be prohibitive.

Collaboration and Coordination with Other Institutions

- Past and ongoing pulsed field gradient NMR electrolyte solution transport property measurements performed by Kee Sung Han (PNNL/EMSL)
- Imaged electrode fabricated by CABS partner (Sergiy Kalnaus, ORNL)
- Pouch cell constructed by Andrew Jansen at ANL's Cell Analysis, Modeling, and Prototyping (CAMP) Facility
- X-ray microtomography imaging performed at ANL's APS 2-BM with assistance from beamline scientist Xianghui Xiao
- "CD-adapco" postprocessing subproject performed by team member Kenneth Higa at LBNL

Remaining Challenges and Barriers

- Voxel-by-voxel comparison between image data sets obtained at different times cannot be done exactly due to slight sample movements as well as changes in electrode thickness
- Reconstructions from APS 2-BM data and using 2-BM reconstruction script with phase contrast retrieval do not provide straightforward quantitative relationship between voxel values and X-ray absorption / material identity, complicating quantitative interpretation of image data

Proposed Future Research

- Image analysis of *in operando* electrode to continue in FY18 to detect further correlations between reconstructed images and electrochemical measurements
  - It may be necessary to assume that voxel intensity and X-ray absorption are approximately correlated in order to perform further quantitative analysis
- New postprocessing pipeline source code to be integrated into our TomPost image postprocessing library (FY18)
- Measurement (Kee Sung Han, PNNL/EMSL) of self-diffusivity for $LiPF_6$ electrolyte solution in EC/EMC (3:7 by mass) solvent mixture, used at CAMP/ANL and now at ORNL, to be processed for use with concentrated solution theory (FY18)
- Ongoing: self-diffusivity measurements at PNNL for LiPF6 in EC/EMC (3:7 by mass),
- The CAEBAT 3 program is not expected to continue into FY19
- Any proposed future work is subject to change based on funding levels.

Summary Slide

- In operando imaging of NMC 532 pouch cell performed at APS 2-BM (fulfilling FY18 imaging milestone)
- New postprocessing pipeline developed to perform alignment of reconstructions at different times (fulfilling FY18 postprocessing milestone)
- Preliminary quantitative analysis of images and electrochemical data suggests that
  - NMC electrode thickness is clearly correlated with SOC only in initial cycles with slow charging
  - Subsequent faster charging cycles are not associated with clear changes in thickness
  - Subtle but consistent changes in electrode voxel value histograms suggest changes in density, to be further explored